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Type of Organization: College or University

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Project Title: Mercury Sequestration: Remediation of Lake Superior Sediment

Project Category: Contaminated Sediments

Rank by Organization (if applicable): 0

Total Funding Requested ($): 183,444 **Project Duration:** 2 Years

Abstract:

Mercury contamination is a ubiquitous problem in the Great Lakes, including the Duluth, MN harbor. Altering the redox conditions in the sediment may prove a useful strategy for sequestering mercury. Sequestration would prevent transport to uncontaminated sites or uptake by bacteria to form the neurotoxin methylmercury. This study will determine appropriate means to stimulate conditions in Lake Superior sediment favorable for the precipitation of mercury in sulfide minerals. Specifically, we will investigate stimulating the growth of sulfate reducing bacteria via electron donor and/or acceptor addition to maximize pore water sulfide concentrations. The outcome of this research will be clear strategies for mercury remediation in Great Lakes sediment.

Geographic Areas Affected by the Project

States:

- [ ] Illinois
- [ ] Indiana
- [ ] Michigan
- [x] Minnesota
- [ ] New York
- [ ] Pennsylvania
- [ ] Wisconsin
- [ ] Ohio

Lakes:

- [x] Superior
- [ ] Huron
- [ ] Michigan
- [ ] Erie
- [ ] Ontario
- [ ] All Lakes

Geographic Initiatives:

- [ ] Greater Chicago
- [ ] NE Ohio
- [ ] NW Indiana
- [ ] SE Michigan
- [ ] Lake St. Clair

Primary Affected Area of Concern: St. Louis River, MN

Other Affected Areas of Concern: All other AOCs with mercury contamination

For Habitat Projects Only:

Primary Affected Biodiversity Investment Area:

Other Affected Biodiversity Investment Areas:

Problem Statement:

Sediments throughout the Great Lakes, including those in the St. Louis Area of Concern (Duluth, MN harbor) are contaminated with mercury (Hg), resulting in fish consumption advisories and potential human and ecological health threats. Hg is readily cycled in the environment, moving through the atmosphere and the troposphere. Few true sinks for Hg exist, although one pathway for Hg removal from the environment is its precipitation in anaerobic sediments as mercuric sulfide solid (HgS). An alternative and perhaps competing fate for Hg in anaerobic sediments is methylation to methylmercury (MeHg). MeHg bioaccumulates and is a powerful neurotoxin; therefore, the formation of MeHg is particularly problematic. The competition between precipitation and methylation is not well understood, which makes it difficult for engineers and environmental managers to formulate strategies to increase the removal of Hg via HgS formation. It is currently known that sulfate (SO42-) addition to the sediment stimulates SO42- reducing bacteria and MeHg formation (Gilmour, et al., 1992). Sulfate reducing bacteria, however, also produce sulfide (S2-) which could react with Hg and allow it to precipitate as HgS. Other techniques for stimulating S2- production from SO42- reducing bacteria while simultaneously limiting Hg methylation have not been explored. The purpose of the proposed study is to investigate the competition of Hg precipitation and methylation and develop new strategies to stimulate Hg precipitation in anaerobic sediments, while limiting MeHg formation.

Proposed Work Outcome:

Experiments are planned that will develop strategies for the enhanced precipitation and removal of Hg from the aqueous phase. This study will provide information that can be used by engineers and coastal managers to remediate Hg contamination in the Great Lakes. Laboratory experiments will be performed to determine how the formation of FeS minerals impacts the precipitation of HgS and the incorporation of Hg into other mineral phases. Three strategies will also be investigated in the laboratory to maximize S2- formation while minimizing Hg methylation by SO42- reducing bacteria. Sediment samples will be obtained from Slip C in the Duluth, MN harbor to isolate sulfate reducing bacteria that have been previously exposed to mercury. The contamination in Slip C has been previously characterized (Crane, 1999).

One potential remediation strategy that will be investigated is the addition of Fe0 to the sediments. Under conditions typical of sediments, Fe0 will corrode and form hydrogen (H2). H2 can serve as a substrate for many anaerobic microorganisms, including SO42- reducing bacteria (Rajagopal and LeGall, 1989; Belay and Daniels, 1990). The Fe0 will provide a slow and steady source of H2 over time. As the SO42- reducing bacteria use the H2, they reduce SO42- to S2-, providing a source of S2- for HgS precipitation. As the Fe0 corrodes Fe2+ is also released. The production of Fe2+ will stimulate abiotic mineral formation, potentially incorporating Hg into the mineral phase and providing another route for Hg removal from solution.

Two additional strategies will also be investigated; these are the addition of FeSO4 and the addition of electron donors for SO42- reduction other than Fe0 (H2). FeSO4 will stimulate SO42- reduction by increasing the amount of SO42- available for reduction by the organisms. It will also provide Fe2+ for mineral formation. The addition of electron donors, Fe0 or other donors such as acetate, will stimulate SO42- reduction and the formation of more S2-.

The rate of SO42- reduciton, MeHg formation, and Hg removal will also be studied in biological SO42- reducing systems. These biological systems will be amended with various quantities of electron donors and SO42- to stimulate SO42- reduction, and the affect of this on Hg speciation will be determined. Recent work has suggested that methyl mercury production decreases as sulfide concentration increases (Benoit, et al., 1999). Thus, the goal of these studies is to determine what strategy allows maximum S2- production, maximum Hg removal (through HgS or incorporation into FeS minerals), and minimum MeHg formation.

Abiotic experiments will be performed with iron sulfide to investigate the potential reactions of mercury with FeS and to assess the competition of Hg2+ and Fe2+ for S2-. The goal of these studies is to determine whether the addition of S2- (via SO42- reduction) and Fe2+ (via direct addition or through Fe0 oxidation) will promote the precipitation and removal of Hg directly (through HgS formation or chemical reduction of mercury) or indirectly (through Hg incorporation or substitution into FeS minerals).

The outcome of these studies will be a clear strategy for engineers and Great Lakes coastal managers for sequestering Hg in sediments. These strategies will consist of which electron donor or acceptor to add, at what relative quantities, and whether Fe2+ (via Fe0 or FeSO4 addition) should be added as well. The Office of Naval Research is currently sponsoring the investigation Fe0 addition in our laboratory for the enhanced degradation of PCBs in sediments.

References

Belay, N.; Daniels, L., 1990. "Elemental Metals as Electron Sources for Biological Methane Formation from CO2" Antonie van Leeuwenhoek, 57, 1-7.

Benoit, J.M.; Gilmour, C.C.; Mason, R.P.; Heyes, A., 1999. "Sulfide Controls on Mercury Speciation and Bioavailablitity to Methylating Bacteria in Sediment Pore Waters" Environ. Sci. Technol., 33, 951-957.

Crane, J.L., 1999. "Assessment of Contaminated Sediments in Slip C, Duluth Harbor, MN," EPA-905-R99-007, U.S. Environmental Protection Agency, Great Lakes National Program Office, Chicago, IL.

Gilmour, C.C.; Henry, E.A.; Mitchell, R., 1992. "Sulfate Stimulation of Mercury Methylation in Freshwater Sediments" Environ. Sci. Technol., 26, 2281-2287.

Rajagopal, B. S.; LeGall, J., 1989. "Utilization of Cathodic Hydrogen by Hydrogen-Oxidizing Bacteria" Appl. Micro. Biotech., 31, 406-412.

Project Milestones:	Dates:
Project Start	09/2000
Sample Collection	10/2000
Method Development	12/2000
Abiotic Experiments	11/2001
Biological Experiments	11/2001
Strategy Optimization	05/2002
Draft Report	06/2002
Project End	/

☐ Project Addresses Environmental Justice

If So, Description of How:

☒ Project Addresses Education/Outreach

If So, Description of How:

The proposed research will be performed by the principal investigators and two graduate research assistants (RAs). The RAs will obtain extensive training in laboratory research methods, specifically on the use of analytical equipment, experimental design, and statistical data analysis methods. In addition, the student will enhance his or her technical writing and oral presentation skills through the preparation of a thesis, reports, and by presenting his or her research at departmental seminars and at local conferences. Results will be disseminated through scholarly publications in peer-reviewed journals such as "Water Research" and "Environmental Science and Technology" and will also be presented at national and regional conferences. The graduate students performing the research will write the manuscripts and present his or her research results. This will aid in the learning process by allowing the student to critically examine his or her own research in light of comments and suggestions from outside parties.

Project Budget:

	Federal Share Requested ($)	Applicant's Share ($)
Personnel:	71,080	13,031
Fringe:	25,469	3,571
Travel:	8,000	0
Equipment:	0	0
Supplies:	24,000	0
Contracts:	0	0
Construction:	0	0
Other:	3,660	0
Total Direct Costs:	132,209	16,602
Indirect Costs:	51,235	7,969
Total:	183,444	24,571
Projected Income:	0	0

Funding by Other Organizations (Names, Amounts, Description of Commitments):

Approximately 13% of the overall project cost will be provided by contributions of cost-shared salary from the two principal investigators (Dr. William Arnold and Dr. Paige Novak).

Description of Collaboration/Community Based Support: